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Title: PREDICTION OF GAS PRESSURIZATION AND HYDROGEN GENERATION FOR SHIPPING HAZARD ANALYSIS: SIX UNSTABLIZED Pu 02 SAMPLES

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Prediction of Gas Pressurization and Hydrogen Generation for Shipping Hazard Analysis: Six Unstabilized Plutonium Oxide Samples

Radiolysis of water to form hydrogen gas is a safety concern for safe storage and transport of plutonium-bearing materials. Hydrogen gas is considered a safety hazard if its concentration in the container exceeds five percent hydrogen by volume, DOE Docket No. 00-11-9965. Unfortunately, water cannot be entirely avoided in a processing environment and these samples contain a range of water inherently. Thermodynamic, chemical, and radiolysis modeling was used to predict gas generation and changes in gas composition as a function of time within sealed containers containing plutonium bearing materials. The results are used in support of safety analysis for shipping six unstabilized (i.e. uncalcined) samples from Rocky Flats Environmental Technology Sits (RFETS) to the Material Identification and Surveillance (MIS) program at Los Alamos National Lab (LANL). The intent of this work is to establish a time window in which safe shipping can occur.

Assumptions: This model assumes that the bulk "impurity" material does not absorb water. If the bulk material absorbs water, then that water will be removed from the majority of the radiolysis field and therefore will undergo radiolysis at a slower rate resulting in a hydrogen pressure smaller than the maximum pressure possible using this model. All of the impurities are being treated as having no interaction with the water; therefore this is a worst case scenario. Since the temperature is unknown, we used a temperature of 315 K (107 ^{o}F). At higher temperatures reaction rates increase yielding a shorter time window for safe shipping. The specific surface area (SSA) for these samples has not been measured. Similar materials have been studied and an average SSA of 5 m^2 g^{-1} was observed.[4] We expect the SSA of these materials to be higher because they have not been calcined. As the surface area increases, the final pressure in the storage container at the end of one year will be less, since more water is used in the construction of the first monolayer which is assumed to be nonreactive.[5] Therefore, we have chosen a SSA of 5 m^2 g^{-1} for these calculations.

Our calculations show that 5 of the 6 items can be packaged and shipped to Los Alamos National Laboratory inside 200 days or less without exceeding the 5% hydrogen by volume limit as specified in Department of Energy's (DOE) Package Certification Approval Record, Docket No 00-11-9965. Calculations of the gas pressure and changes in gas composition were carried out to one year for each of the six containers. Three containers met the DOE's shipping requirements over the entire year, two containers met these requirements for two hundred days, and one container (ID 39-01483A) met the requirements for only 13 days.